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Chapter → Thermodynamics and Thermochemistry

System → Part of Total universe for which energy changes are discussed

↓

represent

Matter (s, l, g) under study

→ amount fixed (mass, moles)

Surrounding → Part of universe around system is called surrounding

Boundary (B) → Region which separates system & surr

B →
- can be real or Imaginary
- flexible or Rigid
- Conducting (Electrical) or Insulator (Electrical)
- Thermally conducting or (Diathermic) — Heat exchange possible
- Thermally insulator (Adiabatic Boundary) — no heat exchange b/w system & surrounding

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Depending upon Boundary, type of system

Open → Matter exchange ✓
Heat exchange ✓

Closed → Matter exchange ✗
Heat " ✓

Isolated → Matter exchange ✗
Heat exchange ✗

No connection with surrounding

Boundary is adiabatic

Property of system

→ applicable for bulk of system | Macroscopic Nature
& not for a single particle (Microscopic nature)

→ Value of property is defined / obtained at thermodynamic Eq^n state ($cond^n$)

At Equilibrium, state change is opposed without any external effect

Total Bulk is defined by single value of any property.

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Properties of System or properties of matter in System.

1) Intensive

- Properties which are independent of amount/mass of Substance in system.

→ If we cut System or matter into 2 equal Halves, value of property does not change

egⁿ elasticity, Refractive Index, density, gas Pressure, Temperature, molarity, Normality, electrode Potential, conductivity, Resistivity, molar heat capacity(s), specific heat capacity, molar Entropy, Molar Internal Energy (U or E), molar Mass (M), Gibbs free Energy (G), molar Enthalpy (H) etc

2) Extensive (or Extrinsic)

→ Those properties whose value depend on amount of Substance in system.

→ Cutting the system in two equal Halves, value of property becomes Half for each half of ~~substance~~ system.

egⁿ → mass, volume, Heat capacity (c), moles, G, S, H, U etc.

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$\boxed{\dfrac{Ext}{Ext} = Intensive}$

$$\boxed{\frac{U \to Ext}{mole \to Ext} = \text{molar Internal Energy } (U_n \text{ or } U_m) \to Int}$$

$$\boxed{\frac{m \to Ext}{V \to Ext} = \text{density (Int.)}}$$

Ext × Ext ≠ Int.

Ext − Ext ≠ Int.

density = $\dfrac{mass}{Volume}$

$\boxed{\text{specific volume} = \dfrac{Volume}{mass} = \dfrac{1}{dens.}}$

specific volume → Int.

Thermodynamic state of system

→ at thermodynamic Eq^n, A state (condition) of Substance (Matter) in system specified by certain measurable macroscopic properties. (Int. or Ext.)

→ properties can be T, P, density, volume etc.

Value of properties for a particular state remains fixed until thermodynamic Eq^n of system is maintained.

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\# When state of system changes from one Eq^n point to another Eq^n point ; value of properties at those states also changes & ~~same~~ those properties ~~at those states~~ also which are dependent only on the present state (irrespective of path taken to reach the state) are called state variables or functions or properties.

\# change in state function or variable
↓
depend only on Initial and final state.

$\Delta T = T_2 - T_1$
↓
change in state function

\# Reversible expansion/compression work → state function

$\boxed{T \rightarrow \text{State function or variable}}$

\# T, P, V etc ⟶ State variable / property

If T is obtained from values of $\boxed{P \& V}$ (Independent variable) for any state then Temp. Becomes state function for that state.
(dependent variable)

\# Path function → Function which depends on path taken to reach from one state of system to another state of system. eg^n → Work, Heat, Heat capacity

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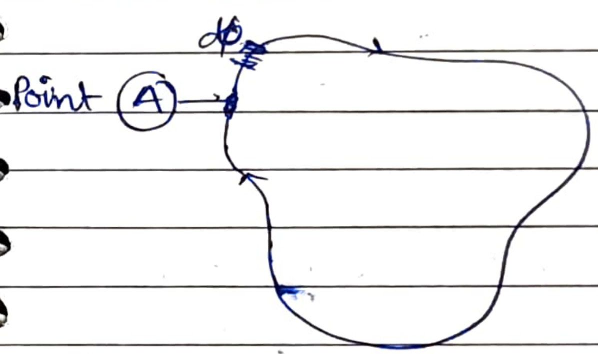
(#) Conditions for function to become State function

① Cyclic Integration is zero

$\boxed{\text{Intial State} = \text{final State}}$

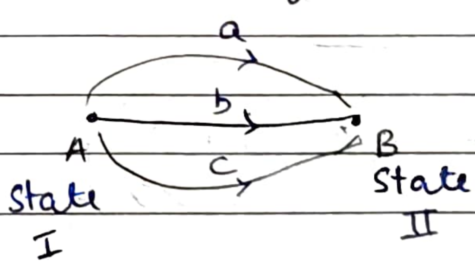
let ϕ is a function

If $\int_A^A d\phi$ or $\oint d\phi = 0$, then ϕ is a State function



② B/w 2 states, change in State function is same for all the path taken

eg^n



let ϕ is a function

for ϕ to be State function

$$(\Delta\phi)_a = (\Delta\phi)_b = (\Delta\phi_c)$$

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(3) Euler's Reciprocity theorem must be satisfied

let ϕ is function of x & y $\Rightarrow \phi = f(x,y)$

~~for ϕ to be state funⁿ~~

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial \phi}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial \phi}{\partial x}\right)_y\right]_x$$

Or

$$\left[\frac{\partial^2 \phi}{\partial x\, \partial y}\right]_{x,y}$$

(1) → Prove Pressure of 1 mole ideal Gas is state function.

Solⁿ $PV = RT$

$P = f(V,T)$

$$\boxed{P = \frac{RT}{V}}$$

To prove :- $\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T$

$-R/V^2$ $-R/V^2$

$$\boxed{\text{Hence Proved.}}$$

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Thermodynamic eq^n

Thermodynamic eq^n → Mechanical Eq^n (No pressure Gradient) — No change in Pressure or force per unit time

↓ Chemical Eq^n

⇓ In Reversible Rx^n :-

↓

No concentration gradient for any species in Rx^n

↳ conc. of every species becomes const. (does not change with time) when Eq^n is achieved

↓ Thermal Eq^n (No temp. gradient)

at this $cond^n$ only we can find value of any macroscopic property in any state of system.

Thermodynamic process :- Any method / process by which system can change its state from one state of thermodynamic Eq^n to another thermodynamic Eq^n.

(**) During the process, value of any macroscopic property cannot be defined.

(**) If process occurs keeping any state property const., then iso prefix is used.

→ Process occur at const. Temp ; Isothermal Process

$T = Const$

$\Delta T = 0$

Small $dT = 0$ — change in Temp.

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→ Process occur at const vol; $\boxed{\text{Isochoric Process}}$ $\Delta V = 0$ $dV = 0$

→ " " " Press. $\boxed{\text{Isobaric Process}}$ $dP = 0$ $\Delta P = 0$

→ $\boxed{\text{Adiabatic process}}$ → No heat exchange b/w system & Surrounding during the process.

$\boxed{Q \text{ or } q = 0}$

→ $\boxed{\text{Cyclic Process}}$ → $\boxed{\text{Initial state = final state}}$

$\boxed{\text{Change in state funct} = 0}$

$\boxed{\text{Work done or heat exchange} \neq 0}$

Classification of thermodynamic processes on the Basis of the way these processes are carried out :-

① Reversible Process

If a process is carried out in such a manner so that the system is always in thermo-dynamic eqn at every stage of the process.

or

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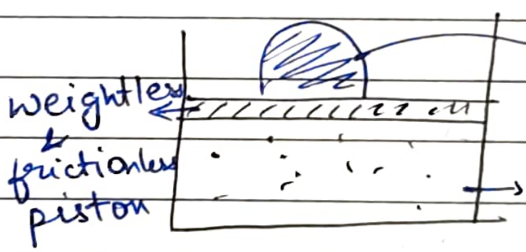
If the process is carried out such that the difference is driving force and opposing is $\boxed{\text{infinitesimally}}$ small. So, that process takes place at infinitesimally slow rate.

↳ negligibly

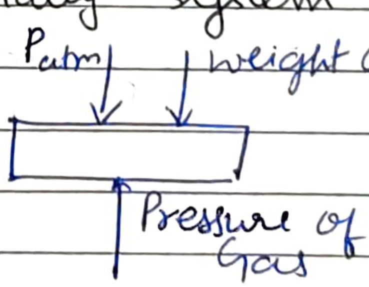
$$\boxed{F_{driving} = F_{opposing} \pm dF} \qquad \boxed{dF \rightarrow 0}$$

\# An ideal Reversible Process will take infinite time for $\boxed{\text{completion}}$ → reaching from initial state to required final state.

\# Let's consider an example ÷



Initially system at Rest (Eq^n)



$$\boxed{P_{atm} + \frac{W}{A} = P_g}$$

↳ Area

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- If one sand particle is removed such that Eq^n is not disturbed b/w system & surrounding

piston moves upwards giving infinitsimally small volume change due to small diff in opposing Pressure (P_{ext}) (External) and Pressure of Gas (driving force)

for negligible expansion of Gas

$$\boxed{P_{ext} = P_{int} - dP} \quad dP \to 0$$

$P_{int} \to P_g$

$dP \to$ very small step of expansion

** If one sand particle is kept on piston, very small compression is observed.

$$\boxed{P_{ext} = P_g + dP} \quad dP \to 0$$

So, for Reversible process at every small step

$$\boxed{P_{ext} = P_g \pm dP}$$

② Irreversible process :-

If process is carried out in such a manner so that the system is in thermodynamic

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equilibrium only at initial and final state of the process.

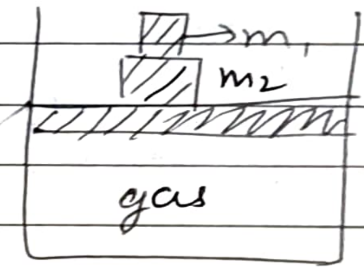
(**) There will be $\boxed{\text{no equilibrium}}$ b/w system & surrounding during process.

(**) Steps are Big involving Big change in macroscopic properties.

(**) Irreversible can be completed in finite steps (1, 2, 3 . . .)

(**) Diff. b/w opposing force & Driving force is finite.

egn



• If m_1 is removed

P_{ext} (opposing Press.) is $P_{atm} + \frac{m_2 g}{A}$

& gas expands under this Pressure $\left[P_{atm} + \frac{m_2 g}{A}\right]$

So, P_{ext} remain const during any step of process.

Initially $P_g = P_{ext}$

$P_{atm} + \frac{m_1 g}{A} + \frac{m_2 g}{A}$

• If m_2 is also removed, ~~gas expands~~ under $\boxed{P_{ext} = P_{atm}}$

till $\boxed{P_g = P_{ext} = P_{atm}}$

★ **Heat and Work** :- Two ways by which system can interact or can exchange energy with its surroundings

Heat :- Energy exchange due to temp. diff b/w syst. & surr.

Work :- Energy exchange takes place not due to temp. diff. but due to difference in opposing force & driving force

Sign convention

q = +ve (Heat absorbed by system)

q = -ve (" released by system)

$\boxed{\text{Chemistry}}$ → we are external (surrounding)

$\boxed{\text{system}}$

(Expansion of Gas)
W. done by system = -ve
W. done by surrounding = +ve
→ (Compression)

$\boxed{\text{Physics}}$ → we are inside system or we are system.

W. done by system = +ve (Expansion)

" " on system = -ve (Compression)

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Internal Energy (E or U)

Sum of all possible ~~value~~ forms of Energy associated with matter in any thermodynamic state of system at given Temp.

Extensive

State function

$U = K.E + P.E + \dots$

$= \text{Translational } K.E + \text{Rotational } K.E + \text{Vibrational } K.E + \text{Attractive Energy} + \text{Repulsive Energies} + \text{Bond Energy} + \dots$

** Energy due to External field effect is not considered

→ gravitational field, magnetic etc.

** Absolute value of U cannot be determined we always find change of U by FLOT. (First law of Thermo.)

for ideal gas,
- No interaction b/w gas molecules (P.E =
- $U = \boxed{K.E} \rightarrow$ only dependent of Temp.
- U is function of T only for Ideal Gas.

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$\boxed{\Delta U = \Delta K.E}$

$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0 = \left(\frac{\partial U}{\partial P}\right)_T}$ for ideal Gas

for Real Gas,

U is function of {T, P, V}

$\left(\frac{dU}{dV}\right)_{T,P} \neq 0$ $\left(\frac{dU}{dP}\right)_{T,V} \neq 0$

Law of equipartition of Energy :-

* Energy equal to $\left(\frac{1}{2}KT\right)$ is associated with each degree of freedom per ideal Gas molecule.

(D.o.f) Degree of freedom or f → No. of ways in which energy of molecule can be distributed.

Types :-

(i) f_T (Translational d.o.f)

(ii) f_R (Rotational dof)

(iii) $\boxed{f_V \text{ (vibrational d.o.f)}}$ → vibratⁿ in Bond occur at High Temp. $\boxed{T \approx 500°C \text{ or above}}$

* $\boxed{\text{Total Dof } (f)}$ for any molecule $= 3\boxed{N}$

$f = f_T + f_R + f_V$

N → No. of atoms in molecules

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at Room Temp, only $f_T + f_R$ exist

$f_T = 3$ → always for every type of gas

a) Monoatomic Gas :-

$f_R = 0$, $f_v = 0$, $\boxed{f_T = 3}$ ⇒ along x, y, z

eg^n → He, Ne, ~~eg^n~~ etc

→ Total D.of $= 3N = 3 \times 1 = 3$

b) Diatomic Gas :- $\boxed{f_T = 3}$ $\boxed{f_R = 2}$ $\boxed{f_v = 1}$

eg^n CO, O_2, Cl_2, Br_2 etc

→ Total D.of $= 3 \times 2 = 6$

c) Triatomic Gas ⟶ Triatomic Linear (Like Diatomic)

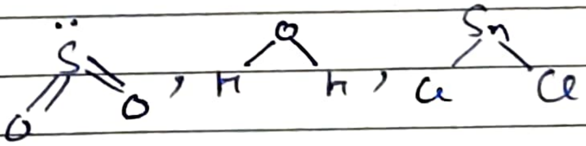
O=C=O, F−Xe−F

CO_2, XeF_2

$f_T = 3$, $f_R = 2$, $f_v = 4$

Triatomic Non-Linear

$f_T = 3$, $f_R = 3$, $f_v = 3$

SO_2 

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d) Polyatomic Gas $\Rightarrow f_T = 3,\ f_R = 3,\ f_V = 3N-6$

Total $= 3N$

for 1 d.of, $\overline{K.E}$ or $E = \frac{1}{2} kT$ per molecule

$= \frac{1}{2} RT$ per mole

at Room Temp.

for f dof, $\overline{K.E} = \frac{f}{2} RT$ per mole of Gas

$\hookrightarrow f_T + f_R$

$= \frac{f}{2} kT$ per molecule

($f_V \rightarrow$ neglected)

$\Delta \overline{K.E} = \Delta U$ (for Ideal Gas)

$\boxed{\frac{f}{2} R(\Delta T) = \Delta U} \rightarrow$ for 1 mole

for n mole of Ideal Gas

$$\boxed{\frac{f}{2} nR\Delta T = \Delta U}$$

$\boxed{f = f_T + f_R}$ $= 3$ (mono)

$= 5$ (Di or Tri linear)

$= 6$ (Tri Non-linear)

Heat (q or Q) :

Energy flow or energy exchange b/w System and surrounding due to Temp. difference

$\boxed{\text{system}}$ ⟹ Temp. of System ↑ed from T_1 to T_2

Heat (q) from surrounding to system is transferred due to temp. difference ($\Delta T = T_2 - T_1$)

T_1 System —q— T_2 surr $\quad T_2 > T_1$

1°C to 2°C → $\Delta T = 1°C$

274K 275K → $\Delta T = 1K$

$$C = \frac{q}{\Delta T} \leftarrow 1°C$$

Heat capacity of Substance in system

$\boxed{\text{Specific Heat capacity (s)}}$ ⟹ $\boxed{s = \frac{C}{\text{mass}}}$

Molar Heat Capacity (C_m)

$$\frac{C}{m/M} = \frac{C}{\text{mole}(n)} = C_m = \frac{q}{n \times \Delta T}$$

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$\boxed{\frac{M.C}{m} = C_n} = \boxed{M.s} \rightarrow$ intensive

Q

$\boxed{\begin{matrix} Al \\ 9g \end{matrix}} \leftarrow 30J$

$25°C$ to $31°C$

$C = \frac{30}{6} = 5\ J/K$ or $5J/°C$

$s = \frac{5}{9}\ JK^{-1}gm^{-1}$

$C_n = \frac{5 \times \cancel{27}^{3}}{\cancel{9}} = 15\ JK^{-1}mol^{-1}$

#

$q \leftarrow \Delta T$ (°C or K)

(Heat capacity) $C = \frac{q}{\Delta T} \leftarrow 1$(°C or K)

⇓

unit = J/K

or

J/°C

→ amount or mass dependent (Extensive)

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Specific Heat capacity of substance (s)

Heat required by substance to change its temp. by 1°C or K for 1 gram substance

$s = \frac{q}{m\Delta T} = \frac{C}{m}$ → Heat capacity ↓ defined for given mass

m ↳ mass of substance

→ Unit → $J(°C)^{-1} gm^{-1}$ or $JK^{-1} gm^{-1}$

Molar Heat Capacity (C_m)

↳ Heat required to change temp. by 1°C. or K for 1 mole substance.

$\boxed{C_m} = \frac{q}{n\Delta T} = \frac{C}{n} = \frac{C}{m} \times M = sM$

n ↳ moles of substance

→ $JK^{-1} mol^{-1}$

$n = \frac{\text{mass (m)}}{\text{Molar mass (M)}}$

Total Heat (q) exchange

$= C\Delta T$

$= ms\Delta T$

$= nC_m\Delta T$

Q → find Total Heat absorbed by 100 g water when it is heated from 25°C to 45°C. s(water) = $4.2\ J(°C)^{-1} gm^{-1}$

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Soln $q = (\overset{m}{100} \times \overset{s}{4.2} \times \overset{\Delta T}{20})\,J$

$= \frac{100 \times 4.2 \times 20}{4.18}\,cal$

$= \frac{100 \times 4.2 \times 20}{1000}\,KJ$

Molar Heat Capacity (C_m) at

Const Volume process $\rightarrow C_{m,v}$ or C_v.

Molar heat capacity (C_m) at

Const Pressure process $\rightarrow C_{m,p}$ or C_p

Molar Heat Capacity $C_m \rightarrow \infty$ (for isothermal) $\Rightarrow \Delta T = 0$

$\rightarrow 0$ (for adiabatic) $\Rightarrow q = 0$

for Solids / liq $\rightarrow C_p \approx C_v$

for gases $\Rightarrow C_v = \frac{q_v}{n\Delta T}$ $\rightarrow$ Heat exchange at const. V

$C_p = \frac{q_p}{n\Delta T}$ $\rightarrow$ Heat exchange at const. P

Meyer's Relation

$\boxed{\text{Relation b/w } C_p \,\&\, C_v}$

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$\boxed{C_p - C_v = R}$ $\boxed{C_p = R + C_v}$

$\frac{C_p}{C_v} = \gamma$ (Poisson's Ratio) $\gamma > 1$ $C_p > C_v$

$\boxed{C_v = \frac{f}{2} R}$

$\boxed{C_p = \left(\frac{f+2}{2}\right) R}$

T = Moderate or Room Temp.

Atomicity of Gas	C_v	C_p	γ
Mono	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3} = 1.67$
Dia or Tri(L)	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.40$
Tri (NL)	$\frac{6R}{2} = 3R$	$\frac{8R}{2} = 4R$	$\frac{4}{3} = 1.33$
Polyatomic	$3R$	$4R$	$\frac{4}{3} = 1.33$

$dq_v = dU$

$\boxed{q_v = \Delta U} = nC_v\Delta T \Rightarrow \frac{f}{2}\cancel{n}R\Delta T = \cancel{n}C_v\Delta T$

$\boxed{C_v = \frac{f}{2}R}$

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$$C_v = \left(\frac{dU}{dT}\right)_V = \left(\frac{dq}{dT}\right)_V$$

$q_p = \Delta H \rightarrow$ Enthalpy change

$$dq_p = dH$$

$$\boxed{\left(\frac{dH}{dT}\right)_p = C_p = \left(\frac{dq}{dT}\right)_p}$$

Heat capacity (C)

- is process dependent
- path function
- Extensive property
- Temp. dependent

Unit: J/°C or J/K

> If Temp. dependency is not given, take Heat capacity of substance as temp. independent.

First law of Thermodynamics (FLOT)

"Energy is always conserved for universe."

or

"Total energy for an isolated system remains constant."

or

"Energy can neither ~~nor~~ be created nor be destroyed, it converts from one form to another form."

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<u>Mathematically,</u>

path dependent

System $\xrightarrow[+\text{work}]{+q\text{ (heat)}}$ System

U_1 (State function) Initially $\qquad U_2$

$$U_1 + q + w = U_2$$

$$U_2 - U_1 = q + w$$

$$\Delta U = q + w$$

$$\boxed{dU = \delta q + \delta w}$$ ⟹ Sum of two inexact differential can be exact differential

or

$$\boxed{dU = dq + dw}$$

At const Volume $\boxed{\text{Isochoric process}}$

$w = 0 \qquad \boxed{\Delta U = q_v}$

Q→ What is change in Internal energy ~~due~~ when 40 KJ work is done on system & 20 KJ heat is released by system?

Sol^n $\quad \Delta U = \boxed{q} + \boxed{W} \rightarrow +40 \quad = -20 + 40 \quad = 20\text{ KJ}$

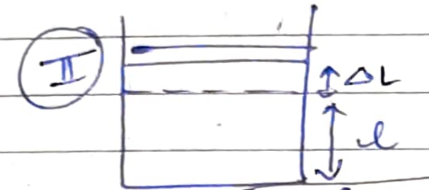
$q \rightarrow -20$

Work

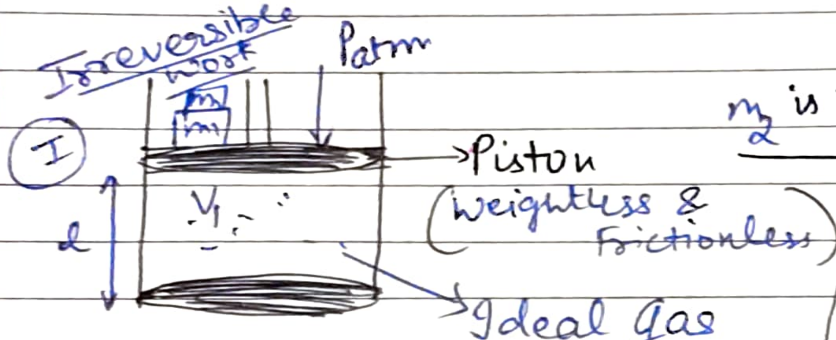
$$W = \boxed{\frac{F}{A}} \times (d \times A)$$

$\frac{F}{A}$ → Pressure

$(d \times A)$ → Volume displaced (for gases)



$\boxed{V_2 = (l + \Delta l) \times A}$



$V_1 = l \times A$

m_2 is removed →

$P_g > (P_{ext})_1$, gas expansion will occur till $\boxed{P_g = (P_{ext})_2}$ & Vol. of gas becomes V_2.

$= \boxed{P_{atm} + \frac{m_1 g}{A}}$

Initially system is in Thermodynamic eq^n.

$$P_g = (P_{ext})_1 = P_{atm} + \frac{(m_1 + m_2)}{A} g$$

$$\boxed{W_{\text{single step}} = -\underbrace{P_{ext}}_{\text{Ext. Press. during that step}} \cdot \underbrace{\Delta V}_{\text{vol. change of Gas in single step}}}$$

$$W_{I \to II} = -(P_{ext})_2 \cdot \Delta V$$

$$= -(P_{ext})_2 \cdot (V_2 - V_1)$$

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(#) Note :- Irreversible single Step work

$$= -P_{ext} \cdot \Delta V$$

$$= -P_{ext}(V_2 - V_1)$$

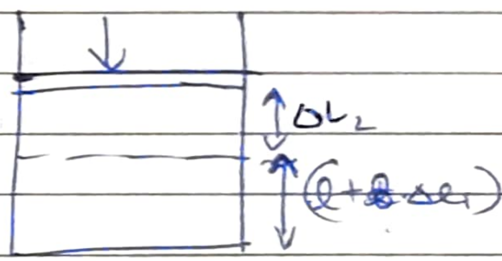
$$= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

If process is complete,

$$\boxed{P_{ext} = P_g}$$

If m_1 is removed $\longrightarrow$ gas expansion occurs (w. done by gas) to achieve $(P_{ext})_3 = P_{atm}$

III



$$V_3 = (l + \Delta l_1 + \Delta l_2) A$$

$$w_{\text{II to III}} = -(P_{ext})_3 (V_3 - V_2)$$

$$= -P_{atm}(V_3 - V_2)$$

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If Both m_1 & m_2 are simultaneously removed then Vol of gas changes from $V_1 \longrightarrow V_3$ under const. ext. Pressure of P_{atm}

$$\boxed{W_{I\ to\ III} = -P_{atm}(V_3 - V_1)}$$

$$\cancel{W_{single\ step} = -P_{ext}\,\Delta V}$$

Note ÷

Irreversible single step work

$$= -P_{ext} \cdot \Delta V$$

$$= -P_{ext}(V_2 - V_1)$$

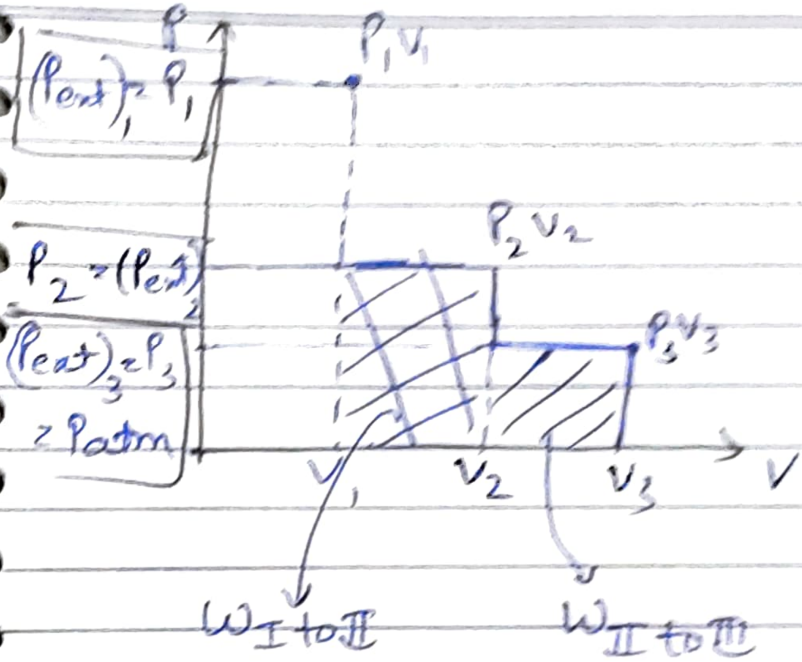
$$= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

If Process is complete

$$\boxed{P_{ext} = P_2}$$

2 step work (Expansion)

$$\underset{P_g = P_1}{(I)} \xrightarrow[\ ]{\text{under } (P_{ext})_2} \underset{P_2, V_2}{(II)} \xrightarrow[\ ]{\text{under } (P_{ext})_3} \underset{P_3, V_3}{III}$$



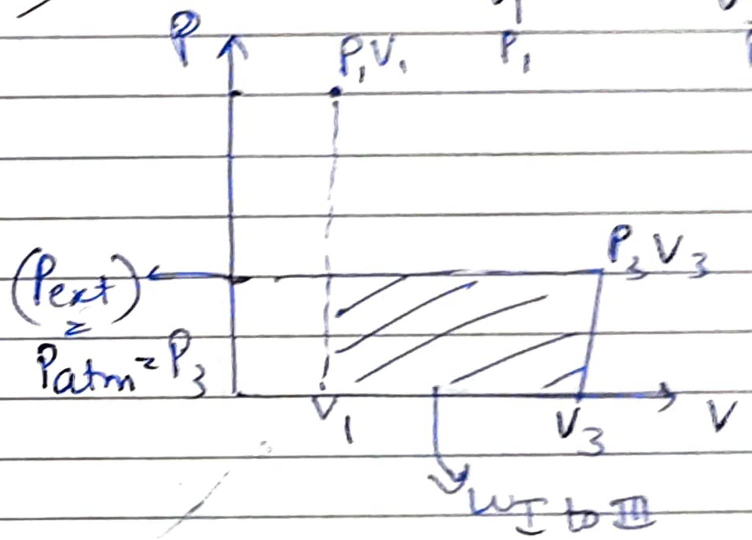
$V_2 > V_1$, $V_3 > V_2$

single step (Expansion) $\quad$ I ——— III

$V_1 \qquad V_3$

$P_1 \qquad P_3$

$\boxed{V_3 > V_1}$



So, During Expansion (Irreversible)

$$|W_{\text{infinite steps}}| \;\ldots\ldots\; \underbrace{|W_{3\,step}| > |W_{2\text{-}step}| > |W_{\text{single step}}|}_{|W_{irr}|\ \text{expansion}}$$

or

$|W_{Rev}|$ expansion

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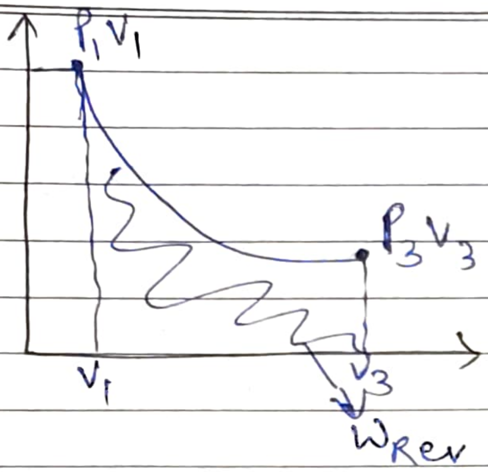

$$\int dW_{Rev} = -\int P_{ext} \cdot dv$$

$$\boxed{P_{ext} = P_g \pm dp} \rightarrow \text{for single step}$$

$$dp \rightarrow 0$$

$$W_{Rev} = -\int_{V_i}^{V_f} (P_g \pm dp)\, dv$$

$$W_{Rev} = -\int_{V_i}^{V_f} P_g\, dv \mp \cancel{\int dp\, dv}^{\,0}$$

$$\boxed{W_{Rev} = -\int_{V_i}^{V_f} P_g\, dv = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dv}$$

works for both Exp. or Compression

Note ÷ Compression of Gas, V ↓es., $\boxed{W = +ve.}$

$$|W_{single\ step}| > |W_{2-step}| > \ldots |W_{infinite\ step}| \text{ or } |W_{Rev}|$$

Spiral

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W-done in Various Process

① Isothermal Process $\Rightarrow$ $T = \text{const.}$ $\Delta T = 0$

$$\Delta U = nC_v \Delta T = 0$$

$\Delta U = 0$

$U = \text{const.}$

$q + w = 0$

$\boxed{q_{iso} = -w_{iso}}$

$$\Delta H = nC_p \Delta T = 0$$

$\Delta H = 0$ $\quad H = \text{const.}$

H & U Both depends only on Temp. for Ideal Gas.

$\boxed{P_i V_i T} \longrightarrow \boxed{P_f V_f T}$

Initial state of ideal gas

final state of ideal gas

ⓐ $$(W_{Rev})_{iso} = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{P_i}{P_f}\right)$$

or

$$= -2.303\, nRT \log\left(\frac{V_f}{V_i}\right)$$

or

$$-2.303\, nRT \log\left(\frac{P_i}{P_f}\right)$$

Boyle's law

$\boxed{P_i V_i = P_f V_f}$

$\boxed{\frac{V_f}{V_i} = \frac{P_i}{P_f}}$

Spiral

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$$\boxed{(q_{iso})_{rev} = (-W_{iso})_{Rev}}$$

Q → find q, ΔU, W when 2 mole of ideal undergoes Reversible isothermal process to change its state from (1 atm, 300K) to (3atm, 300K)?

$R = 0.0821$ or $\frac{1}{12}$ L-atm mol^{-1} K^{-1}

Soln

$\Delta U = 0$

$q_{rev} = -W_{rev}$

$$W_{Rev} = -2.303\ nRT \log\left(\frac{P_i}{P_f}\right)$$

$$= -2.303 \times 2 \times 0.0821 \times 300 \times \log\left(\frac{1}{3}\right)$$

$$= +2.303 \times 2 \times 0.0821 \times 300 \times 0.47 \text{ l-atm}$$

1 L-atm = 101.325 Joule

log 2 = 0.3
log 3 = 0.47
log 5 = 0.7
log 7 = 0.84
log 11 = 1.043

$(W_{Rev})_{compression}$

$= 2.303 \times 2 \times 0.0821 \times 300 \times 0.47$

$\times 101.325$ Joules

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(b) Single step

$$W_{irr} = -P_{ext}(V_f - V_i)$$

$$= -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

$$(W_{irr})_{iso} = -P_{ext}\, nRT\left[\frac{1}{P_f} - \frac{1}{P_i}\right]$$

** When Exp. or compression completes

$$\boxed{P_{ext} = P_f}$$

$$\boxed{(W_{irr})_{iso} = -nRT\left[1 - \frac{P_f}{P_i}\right]}$$

Q→ find ΔU when 20 KJ heat is given to ideal Gas & gas expands under Ext Press. of 2 atm from 3 dm^3 to 5 dm^3?

Soln

$$\Delta U = q + w$$

$$\Delta U = 20 - P_{ext}\Delta V$$

$$= 20(KJ) - \underbrace{2(5-3)}_{l\text{-}atm}$$

$$\Delta U = 20\times10^3 (J) - (2\times2\times101.325)\,J$$

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② Adiabatic Process $\boxed{P_1V_1T_1 \longrightarrow P_2V_2T_2}$

⇒ System having ideal Gas is isolated

⇒ $q = 0$ → Heat exchange = 0

⇒ $\Delta U = \cancel{q}^{0} + w$

$$\boxed{\Delta U = W_{ad} = nC_V(T_2 - T_1)} \rightarrow \boxed{\text{Rev or Irr.}}$$

$$C_p - C_V = R$$

$$\frac{C_p}{C_V} - \frac{C_V}{C_V} = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V}$$

$$\boxed{C_V = \frac{R}{(\gamma - 1)}}$$

$$W_{ad} = \frac{nR}{(\gamma-1)}\left[\frac{P_2V_2}{nR} - \frac{P_1V_1}{nR}\right]$$

$$\boxed{W_{ad} = \frac{P_2V_2 - P_1V_1}{(\gamma - 1)} = \frac{\Delta(PV)}{(\gamma-1)}}$$

Adiabatic Exp. of Gas

↳ $W_{ad} = -ve$

$$nC_v(T_2 - T_1) = -ve$$

$T_2 < T_1$ T ↓es, Cooling

Adiabatic Compression of Gas

$W_{ad} = +ve$

$\Delta T = +ve$

$T_2 > T_1$ T ↑es, Heating

If During Calculation of Work, any parameter is not given then, we must know whether Process is Rev. or Irr.

(a) Process is Rev. Ad.

$$dU = (dW_{ad})_{Rev}$$

$$nC_v\,dT = -\int nRT\frac{dV}{V}$$

$$nC_v\int\frac{dT}{T} = -nR\int\frac{dV}{V}$$

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$$nC_v \ln\left(\frac{T_2}{T_1}\right) = -nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = (\gamma-1) \ln\left(\frac{V_2}{V_1}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\boxed{TV^{\gamma-1} = \text{const.}}$$

Similarly,

$$\boxed{PV^{\gamma} = \text{const.}}$$

$$\boxed{T^{\gamma} P^{1-\gamma} = \text{const.}}$$

(b) Irr. Ad

$$\Delta U = W_{ad}$$

$$nC_v(T_2 - T_1) = -P_{ext}(V_2 - V_1)$$

$$\boxed{nC_v(T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)}$$

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Q → 3 mole of non-linear triatomic Gas undergoes adiabatic process such that state of Gas changes from

$\boxed{16\,atm, 300K} \longrightarrow \boxed{1\,atm, T(K)}$

find T & work if (i) Process is Reversible

(ii) Process is Irreversible

Solⁿ (i) Reversible

$W_{ad} = nC_v(T_2 - T_1) = 3 \times 3R\,[T - 300]$

T value for Reversible Process

$T^{\gamma} P^{1-\gamma} = const.$

$T_1^{\gamma} P_1^{1-\gamma} = T_2^{\gamma} P_2^{1-\gamma}$

$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{1-\gamma} \Rightarrow T_2 = T_1\left[\frac{P_1}{P_2}\right]^{\frac{1-\gamma}{\gamma}}$

$T = T_2 = 300\left[\frac{16}{1}\right]^{\frac{1-\frac{4}{3}}{\frac{4}{3}}}$ $= -\frac{1}{4}$

$= 300\,(2^4)^{-1/4}$

$= \frac{300}{2} = \boxed{150K}$

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$(W_{ad})_{Rev} = 3 \times 3R[150-300] = 9R \times (-150)$ Joules

(ii) <u>Process is Irr.</u>

$(W_{ad})_{irr} = 3 \times 3R(T-300)$

T is calculated from irreversible path using Eq^n (1) or (2)

$$-1 \times R\left[\frac{T}{1} - \frac{300}{16}\right] = 3R[T-300]$$

$$\boxed{T \approx 230\,k}$$

$$(W_{ad})_{irr} = 3 \times 3R(T-300)$$
$$= 3 \times 3R(230-300)$$
$$= 9R(-70)$$

(cooling)

Conclusion

Initial state

$$\begin{tikzcd} P_1V_1T_1 \arrow[r, "\text{Adiabatic}", "\text{Rev. Exp.}"'] \arrow[d, "\text{Ad Irr Exp}", "\text{cooling}"'] & P_2V_2(T_{Rev})_{final} \\ P_2V_2,(T_{Irr})_{final} & \end{tikzcd}$$

$$|(\Delta T)_{Rev}| > |(\Delta T)_{Irr}|$$

$(\Delta T)_{Rev}$

$$\boxed{\underbrace{T_1 > (T_{irr})_{final}}_{(\Delta T)_{irr}} > (T_{Rev})_{final}}$$

Date ....

Comparision b/w Iso & Adiabatic

Expansion $|W_{iso}| > |W_{Ad}|$ (Rev. or Irr.)

3. Isochoric Process

$V = const.$

$\Delta V = 0$

$\boxed{W = 0}$

from FLOT

$q + w = \Delta U$

$\boxed{q_v = \Delta U} = nC_v\Delta T$

4. Isobaric Process

$P = const.$

$dw = -P_{ext} \, dV$

$w = -P \int dV$

$W = -P\Delta V$

$\boxed{W = -P\Delta V}$

$W = -nR\Delta T$ → gas undergoes expansion or compression

for Rx^n

$T, P, \cancel{V}$ → kept const. when we set any Rx^n.

Work done in case of Rx^n is due to change in

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moles of Gaseous Species:

$$\boxed{W = -P\Delta V = -(\Delta n_g)RT}$$

Q→ find work done in (Joule) when 2 mole Zn is dissolved in HCl in 25° C? $\boxed{R = 8.314\ J/k/mole}$

Soln

$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

2 mole — 2 mole

W. done by system = W. done by H_2 gas = $-\Delta n_g RT$

$= (2-0) \times R \times T$

initial moles of H_2

final moles of H_2

Q-101
(Pg-48)

$Fe(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$

1 mole — 1 mole

$\frac{50}{55.85}$ mole — $\frac{50}{55.85}$

$W = -\Delta n_g RT$

$= \frac{50}{55.85} \times 8.314 \times 298$ Joule

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H (Enthalpy)

- State function
- Extensive property
- Defined as $\boxed{H = U + PV}$

$$dH = dU + d(PV)$$
$$dH = \underbrace{dU + PdV} + V\,dP \xrightarrow{} 0 \text{ at const. } P$$

from FLOT

$$dq + dw = dU$$
$$dq_p - PdV = dU$$
$$\boxed{dq_p = dU + PdV}$$
at const. P

$$\boxed{dH = dq_p} \Rightarrow \boxed{q_p = \Delta H}$$

heat exchange b/w system & surrounding at const P is enthalpy change

a) Nothing is const.

$$\boxed{dH = dU + d(PV)}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

for ideal gas

$$\Delta H = \Delta U + (nRT_2 - nRT_1)$$

$$\boxed{\Delta H = \Delta U + nR(T_2 - T_1)}$$

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b) at const P, $\boxed{\Delta H = \Delta U + P\Delta V}$

Ideal Gas undergoing any Process (Exp or Comp.)

$\boxed{\Delta H = \Delta U + nR\Delta T}$

c) for Rx^n involving Ideal Gases

$\boxed{P\Delta V = \Delta n_g RT}$

$\boxed{\Delta H = \Delta U + \Delta n_g RT}$

$\boxed{\Delta H - \Delta U = \Delta n_g RT}$

$\boxed{q_p - q_v = \Delta n_g RT}$

Q $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -100$ KJ/mole

a) find $\boxed{\text{heat evolved at const. Volume}}$ at 300k?

$q_v = \Delta U$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta U = \Delta H - \Delta n_g RT$

→ Difference of stoichiometric coeff. of product & reactant

$\Delta n_g = 2 - (3+1)$
$= -2$

$\Delta U = \Delta H + 2RT$
$= [-100000 + 2 \times 8.314 \times 300]$ Joule

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b) find heat evolved at const. Volume when 4 moles of N_2 and 12g of H_2 reacts at 300k?

$1N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -100$ kJ/mole

Acc. to stoich. coeff. of (L.R)

N_2	H_2	NH_3
4 mole	$\frac{12}{2} = 6$ mole	0
-2	-6	$+4$
2	0	4

$$\Delta U = \Delta H - \Delta n_g RT$$

$$\Delta U = [-100 \times 10^3 - (-2)RT]$$

→ w.r.t 3 moles of L.R

w.r.t 3 mole of L.R $\longrightarrow \Delta U = [-100 \times 10^3 + 2RT]$

" 1 mole " " $\longrightarrow \Delta U = \left[\frac{-100 \times 10^3 + 2RT}{3}\right]$

" 6 mole " " $\longrightarrow \Delta U = \frac{(-100 \times 10^3 + 2RT)}{3} \times 6$

Thermochemistry

→ We will deal with ΔH of various Rx^ns/phase change

$\Delta H_{Rx} = -ve$ (Exo)

$\Delta H_{Rx} = +ve$ (Endo)

I) Std. Enthalpy of formation (ΔH_f°)

Standard state

Temp. usually taken 25°C	P = 1 bar & Conc = 1 molar

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Enthalpy change (usually −ve) when 1 mole substance (s, l, g) is formed from its constitu-
-ent elements present in their most stable form at std. state.

$$\boxed{\Delta H_f^\circ \text{ (Elemental form)} = 0}$$

- ΔH_f° (C, s, graph.) = 0
- ΔH_f° (C, s, diamond) ≠ 0
- ΔH_f° (H_2, g) = 0
- ΔH_f (H, g) ≠ 0
- ΔH_f° (S_8, rhombic) = 0
- ΔH_f° (S_8, Monoclinic) ≠ 0

rhombic is more stable than Mono-clinic form at RT (25°C)

ΔH_f° (H^+, aq.) = 0 (Assume)

ΔH_f° (OH^-, aq.) ≠ 0

- ΔH_f° (Br_2, l) = 0
- ΔH_f° (Br_2, g) ≠ 0
- ΔH_f° (Cl_2, g) = 0
- ΔH_f° (Cl, g) ≠ 0
- ΔH_f° (O_2, g) = 0

Exception

ΔH_f° (White P) = 0
ΔH_f° (Red P.) ≠ 0
ΔH_f° (Black P) ≠ 0

stability order = White P < Red P. < Black P

$$6C(s,\text{graphite}) + 3H_2(g) \longrightarrow 1\,C_6H_6(l)\ ;\ \Delta H^\circ_{Rx} = -x \text{ kJ/mole}$$

$$= \Delta H_f^\circ (C_6H_6, l)$$

$$-x = \Delta H_{Rx} = 1\,\Delta H_f(C_6H_6) - [\cancel{6\Delta H_f(C, s\,graph)}^{0} + \cancel{3\Delta H_f(H_2)}^{0}]$$

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Note : for any Rx^n

$$\boxed{\Delta H_{Rx} = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})}$$

Q find ΔH_f (C_6H_6)?

$\Delta H_f(C, s, \text{Diamond}) = -x$ KJ/mole

Rx^n is $\rightarrow$ $\boxed{3C(s, \text{Diamond}) + \frac{3}{2}H_2(g) \rightarrow \frac{1}{2}C_6H_6(l); \ \Delta H_{Rx} = -y}$

Sol^n $\Delta H_{Rx} = -y = \frac{1}{2}\Delta H_f(C_6H_6) - 3\Delta H_f(C, s, \text{diamond}) - \frac{3}{2}\cancel{\Delta H_f}(H_2, g)$ $\rightarrow 0$

$$-y = \frac{1}{2}\Delta H_f(C_6H_6) - 3(-x)$$

$$\boxed{2(-3x - y) = \Delta H_f(C_6H_6)}$$

(2) ΔH_c° (Std. Enthalpy of combustion)

↳ Enthalpy change (usually -ve) when 1 mole substance (s, l, g) is completely burnt in oxygen at Std. state.

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ΔH_c = +ve only for F_2, N_2, N_2O

$\Delta H_c(O_2) = 0$
$\Delta H_c(CO_2) = 0$
$\Delta H_c(H_2O) = 0$

$\boxed{1C(s, \text{graphite})} + O_2(g) \rightarrow CO_2(g)$;

$\Delta H_R^\circ = -x = \Delta H_c^\circ(C, s \text{ graphite})$
$= \Delta H_f^\circ(CO_2, g)$

Note :- for any Rx^n

$$\boxed{\Delta H_R = \Sigma \Delta H_c(\text{Reactants}) - \Sigma \Delta H_c(\text{Products})}$$

$\Delta H_R = \Delta H_c(C, s, \text{grap.}) + \cancel{\Delta H_c(O_2)}^{0} - \cancel{\Delta H_c(CO_2)}^{0}$

Q→ $\Delta H_f(C_6H_6, l) = ?$

$\Delta H_c(C_6H_6, l) = -x$

$\Delta H_c(H_2, g) = -y$

$\Delta H_c(C, s, \text{graphite}) = -z$

Sol^n $6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$; $\Delta H_{r x^n} = ?$

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$6\Delta H_c(C,s) + 3\Delta H_c(H_2) - \Delta H_c(C_6H_6) = 1 \times \Delta H_f(C_6H_6)$
$- [\cancel{6\Delta H_f(C,s)} + \cancel{3\Delta H_f(H_2)}]$

$6(-z) + 3(-y) - (-x) = \Delta H_f(C_6H_6)$

$$\boxed{-6z - 3y + x = \Delta H_f(C_6H_6)}$$

Q→ $\Delta H_c(C_6H_6, l) = ?$

$\Delta H_f(CO_2) = -x$

$\Delta H_f(H_2O) = -y$

$\Delta H_f(C_6H_6) = -z$

$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$

$\Delta H_c(C_6H_6, l) = 6\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - \Delta H_f(C_6H_6)$
$- \cancel{\Delta H_f(O_2)}^{0}$

$= 6(-x) + 3(-y) - (-z)$

$= -6x - 3y + z$

Q If x gm Benzene on combustion releases y kJ of heat. find enthalpy of combustion of Benzene?

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Sol^n $\left(\frac{x}{\text{Molar mass of Benzene}}\right)$ moles $\longrightarrow -y$ kJ

1 mole $\longrightarrow \frac{-y}{x/M} \Rightarrow \boxed{\frac{-yM}{x}}$ kJ/mole

ΔH_c (Benzene)

$\boxed{\text{Calorific value (CV)}}$ of substance

Unit J/g or kJ/g or Cal/g

↳ Heat evolved by combustion of 1 gm substance.

** C.V of substance $= \frac{\Delta H_c \text{ (Substance)}}{\text{Molar mass of substance}}$

Q→ ΔH_c (ethanol) $= -x$ kJ/mole
C_2H_5-OH
find C.V of ethanol?

Sol^n 1 mole $\longrightarrow \Delta H_c = -x$
↳ 46 g

$1g \longrightarrow \left(\frac{-x}{46}\right) = C.V$

(3) $\Delta H^\circ_{\text{neutralization}}$ = -ve

$\boxed{\text{Std. enthalpy change}}$ when 1 equivalent or 1gm-eq. Acid is neutralised by 1 gm-eq of Base.

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gm - eq or eq = mole X n.f

$\boxed{\text{equivalent of Strong Acid} = \text{eq of } H^+ = \text{mole of } H^+ \\ \text{equivalent of Strong Base} = \text{eq of } OH^- = \text{mole of } OH^-}$

eq. = N X V_{sol^n} (L) $\boxed{N = M \times nf}$

meq. = N X V_{sol^n} (ml)

$\boxed{\text{1eq. Acid (strong)}}$ + $\boxed{\text{1eq. Base (strong)}}$ → Salt + water

1eq^n H^+ or 1 mole H^+

1eq. OH^- or 1 mole OH^-

$\Delta H^o_{neut} = -57.1$ kJ/mole or kJ/eq or -13.7 kcal/mol

Strong Acid ⇒ $HClO_4$, HI, HBr, H_2SO_4, HCl, HNO_3

Strong Base ⇒ NaOH KOH, RbOH, CsOH $\boxed{Ca(OH)_2 (aq.)}$, $Sr(OH)_2$, $\boxed{Ba(OH)_2}$

↳ Lime water

↳ Baryta water

Q $\Delta H = ?$

1) $\boxed{\text{2 mole NaOH}}$ + $\boxed{\text{1 mole } H_2SO_4}$

2eq. OH^-

2eq. H_2SO_4 = 2eq. H^+

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Solⁿ $\Delta H = (-57.1 \times 2)$ kJ

2) $\boxed{2\ eq\ H_2SO_4}$ + $\boxed{2\ mole\ Ca(OH)_2}$

$\downarrow$ $2\ eq\ H^+$ $\quad$ $\downarrow$ $4\ eq.\ OH^{\ominus}$

$\Delta H = (-57.1 \times 2)$ kJ

3) 100 ml, 0.1 M HCl + 100 ml, 0.1 N $Ca(OH)_2$

↳ 0.1 N

meq $(Ca(OH)_2)$ = meq (OH^-)
= 10 meq.

meq (HCl) = meq (H^+) = 100×0.1
= 10 meq

$$\boxed{\Delta H = -57.1 \times \frac{10}{1000}\ kJ}$$

→ 10 meq.

Q→ find rise in temp. when 100 ml, 0.1 M NaOH reacts with 100 ml, $\boxed{0.1M}$ H_2SO_4 ?

↳ 0.2 N → 20 meq.

$\boxed{\begin{array}{l} s(\text{water}) = 4.2\ JK^{-1}\ gm^{-1} \\ \rho_{H_2O} = 1 g/ml \end{array}}$

$\boxed{q_p = \Delta H} = ms\Delta T$
$= nC\Delta T$

$V_{H_2O} = 200$ ml

$\rho_{H_2O} = \frac{m}{V_{H_2O}}$ $\boxed{m = 200 g}$

$\Delta H = \left| -57.1 \times \frac{10}{1000} \times 1000\ J \right|$ = heat absorbed by water

$\left| -57.1 \times 10 \right| = m \times s \times \Delta T$

$$\boxed{\frac{571 \times 10}{200 \times 42} = \Delta T}$$

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(4) Enthalpy of ionization (ΔH_i)

heat or Enthalpy (+ve) change to convert or dissociate 1 mole weak electrolyte (Weak Acid or Weak Base) completely into ions

ΔH_i ($\underbrace{\text{strong, Electrolyte}}_{\text{S.A, S.B, all Salt}}$) = 0

ΔH_i (Weak Electrolyte) $\neq 0$

Q→ ΔH_i (CH_3COOH) = ?

if 1 mole of CH_3COOH is mixed with 1 mole NaOH & heat of neutralization is −48.1 kJ.

Solⁿ CH_3COOH + $NaOH$ ⟶ −48.1 kJ/mole
1 mole   1 mole

$\Delta H_i = +x$ kJ/mole $\Delta H_i = 0$

1 mole H^+ + 1 mole OH^- ⟶ −57.1 kJ/mole

or

$\downarrow +x$

1 mole H^+ + 1 mole OH^- ⟶ −57.1 ⟹ −48.1

$x + (-57.1) = -48.1$

$\boxed{x = 9 \text{ kJ/mole}}$

Pg-64

Q-5)

Sol^n $\overset{1\ mole}{1\ H_2C_2O_4} + NaOH \longrightarrow$

$\Delta H_i = x$

2 mole H^+

$(2\ eq^n\ H^+) + 2\ eq\ OH^- \longrightarrow -57.1 \times 2$

$$\boxed{x - (-57.1 \times 2) = (-53.35 \times 2)}$$

$$\boxed{x = 8}$$

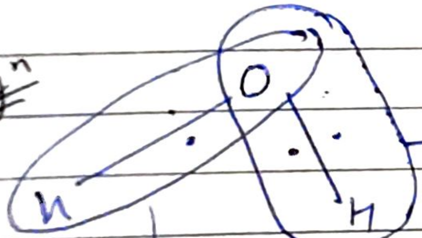
Concept of $\boxed{\text{Bond dissociation ethalpy}}$ and $\boxed{\text{Bond energy}}$

B.E $\Rightarrow$ Average Energy required to Break 1 mole Bond

B.D.E $\rightarrow$ Energy required to Break 1 mole of any covalent Bond.

B.E (Bond Enthalpy) is used when any Bond in repeated more than once in any compound.

eg^n



$\rightarrow B.d.e_2\ (O-H) = x_2$

B.d.e$_1$ (OH - Bond) $= x_1$

$$B.E\ (O-H) = \frac{B.d.e_1 + B.d.e_2}{2} = \frac{x_1 + x_2}{2}$$

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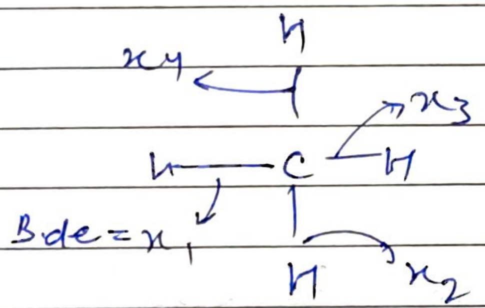
Note ÷ ΔH_a (Enthalpy of atomization)

enthalpy change when 1 mole of any substance (s, l, g) is completely converted gaseous atoms.
(+)

eg^n $CH_4(g) \longrightarrow C(g) + 4H(g)$; $\Delta H_{Rx} = \Delta H_a(CH_4)$



$= x$ KJ/mole

$= x_1 + x_2 + x_3 + x_4$

$$B.E(C-H) = \frac{x_1 + x_2 + x_3 + x_4}{4}$$

$$= \frac{x}{4} = \frac{\Delta H_a(CH_4)}{4}$$

Note ÷

(#) $I_2(s) \longrightarrow I_2(g)$; $\Delta H_{Rx} \neq \Delta H_a(I_2, s)$

$\Delta H_{Rx} = \Delta H_{\text{Sublimation}}(I_2, s)$

(#) $C(s) \rightarrow C(g)$; $\Delta H_R = \Delta H_a(C, s) = \Delta H_{sub}(C, s)$

Note ÷ ΔH of any Rx^n can be represented in terms of B.E data of Reactants and Products (Provided Reactants & Products are present in Gaseous state)

Date ....

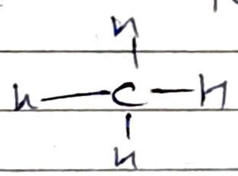
$$\boxed{\Delta H_{Rx} = \sum B.E \text{ data of Reactants} - \sum B.E \text{ data of Products}}$$

Q Combustion of CH_4

$\Delta H_c(CH_4) = ?$

Given :- $B.E\ (C-H) = x_1$ kJ/mole
$B.E\ (O=O) = x_2$,,
$B.E\ (C=O) = x_3$,,
$B.E\ (O-H) = x_4$,,
$\Delta H_{vap}\ (H_2O, l) = x_5$,,

Sol^n $1\ CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$



$\Delta H_{Rx} = \Delta H_c(CH_4) = ?$

$$\Delta H_c(CH_4) = \Delta H_{Rx} = 4B.E(C-H) + 2B.E(O=O) - \left[2B.E(C=O) + 2\Delta H_{vap}(H_2O) + 4B.E(O-H)\right]$$

Laws of Thermochemistry :-

(1) Lavosier law $\rightarrow$ Reversing the rx^n Enthalpy change sign reverses

$A + B \longrightarrow C$; $\Delta H = -x$, Exo
$C \longrightarrow A + B$; $\Delta H = +x$, Endo

Spiral

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(2) $A \rightarrow B \ ; \Delta H_1 = x$

$2A \rightarrow 2B \ ; \Delta H_2 = 2x = 2\Delta H_1$

Imp.

(3) Hess's law → The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps.

eg: 2steps

$$\boxed{\begin{array}{ll} A \rightarrow B & \Delta H_1 = x_1 \\ B \rightarrow C & \Delta H_2 = x_2 \end{array}}$$

$$A \xrightarrow{\Delta H_1} B \xrightarrow{\Delta H_2} C \xrightarrow{\Delta H_3} D$$

$x = \Delta H_{net} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\boxed{A \rightarrow C}$ 1st step

$\boxed{\Delta H = \Delta H_1 + \Delta H_2 = x_1 + x_2}$

Q $\Delta H_c(C_6H_6, l) = ?$

given :- $\Delta H_f(H_2O, l) = -x$
$\Delta H_f(CO_2; g) = -y$
$\Delta H_f(C_6H_6, l) = -z$

→ $1C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta H_{Rx} = \Delta H_c(C_6H_6)$

$\Delta H_c(C_6H_6) = -3x - 6y + z$

Soln Combustion of Rxn for C_6H_6

eq(1). $1C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \ ; \Delta H_{Rx} = \Delta H_c(C_6H_6)$

Date ....

Given : H_2O formation :

eq^n (I) $\left(H_2 + \frac{1}{2}O_2 \longrightarrow 1H_2O(l)\ ;\ \Delta H_f(H_2O) = -x\right) \times 3$

eq^n (II) $3H_2 + \frac{3}{2}O_2 \rightarrow 3H_2O(l)\ ;\ \Delta H_3 = -3x$

CO_2 formation

eq^n (III) $\left(C(s) + O_2(g) \rightarrow 1CO_2(g)\ ;\ \Delta H_f(CO_2, g) = -y\right) \times 6$

$6C(s) + 6O_2 \rightarrow 6CO_2\ ;\ \Delta H_1 = -6y$

C_6H_6 formation :

eq^n (IV) $6C(s) + 3H_2(g) \longrightarrow 1C_6H_6(l)\ ;\ \Delta H_f(C_6H_6) = -z$

Reverse Eq IV

eq IV $C_6H_6 \longrightarrow 6C + 3H_2$ $\boxed{\Delta H_2 = +z}$

Add eq^n III + Eq^n IV + Eq^n II

$\cancel{3H_2} + \frac{3}{2}O_2 + \cancel{6C} + 6O_2 + C_6H_6 \longrightarrow 3H_2O + 6CO_2 + \cancel{6C} + \cancel{3H_2}$

$\Delta H_c(C_6H_6) \Rightarrow \Delta H_{net} = -3x - 6y + z$

$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 3H_2O + 6CO_2\ ;\ \boxed{\Delta H_c = -3x - 6y + z}$

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③ Enthalpy of Hydration of Compound (ΔH_{hyd})

no water

Enthalpy change when 1 mole of a given anhydrous or partially Hydrated Salt is allowed to combine with required no. of moles of water molecules to form a specific stable Hydrated Salt (solid).

stable

eg^n $1 CuSO_4 (s) + 5H_2O (l) \rightarrow \boxed{CuSO_4.5H_2O}$ (solid)

anhydrous Salt

; $\Delta H_{hyd} (CuSO_4, s) = -x$ kJ/mole

$CuSO_4.3H_2O (s) + 2H_2O(l) \longrightarrow CuSO_4.5H_2O (s)$

partially Hydrated

; $\Delta H_{hyd} (CuSO_4.3H_2O, s) = -y$ kJ/mole

$$\boxed{|-x| > |-y|}$$

(when compound is solid)

④ Enthalpy of solution or dissolution:-

can be anhydrous partially Hydrated or completely Hydrated

Enthalpy change 1 mole of substance is completely dissolved in Excess of solvent.

eg^n $CuSO_4(s) + H_2O(l) \longrightarrow CuSO_4(aq)$; $\boxed{\Delta H_{sol} \text{ or } \Delta H_{diss} (CuSO_4, s) = -z}$

Excess

or

$CuSO_4 (nH_2O)$

or

$Cu^{2+}(aq) + SO_4^{2-}(aq)$

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$CuSO_4(s)$ $\quad$ $CuSO_4.3H_2O(s)$ $\quad$ $CuSO_4.5H_2O(s)$

$$CuSO_4(s) \xrightarrow[H_2O]{Excess} CuSO_4(aq.)$$

$$CuSO_4.3H_2O(s) \xrightarrow{H_2O(xs)} CuSO_4(aq.)$$

$$CuSO_4.5H_2O(s) \xrightarrow{H_2O(xs)} CuSO_4(aq.)$$

$Cu^{2+}(aq)$ $\quad$ $SO_4^{2-}(aq.)$

$$\underset{1\,mole}{CuSO_4.5H_2O(s)} + \underset{Excess}{H_2O(l)} \longrightarrow CuSO_4(aq.);$$

$\Delta H_{soln}(CuSO_4.5H_2O,s)$
$= -40$ kJ/mole

Q → $\Delta H_{soln}(CuSO_4.5H_2O, s) = -x_1$ kJ/mole

$\Delta H_{soln}(CuSO_4, s) = -x_2$ kJ/mole

$\Delta H_{hyd}(CuSO_4, s) = ?$

$$CuSO_4.5H_2O(s) \xrightarrow[xs]{\Delta H_1 = -x_1 \quad H_2O} CuSO_4(aq.)$$

$$CuSO_4(s) \xrightarrow{\Delta H = ?} CuSO_4.5H_2O(s)$$

$$CuSO_4(s) \xrightarrow{\Delta H = -x_2} CuSO_4(aq.)$$

$\Delta H + \Delta H_1 = \Delta H_2$

$\Delta H - x_1 = -x_2$

$$\boxed{\Delta H = x_1 - x_2}$$

Date ....

☆ Spontaneous Process

→ are those process which occur own its own without any constant external support.

→ Can be intiated.

→ Irreversible (proceed in one direction)

→ Can be fast or slow.

→ egⁿ (i) all Natural processes.
(earthquake, rain, increase in Height of mountain)

(ii) Diffusion of Gas
(iii) Mixing of Gas
(iv) waterfall
(v) Burning of Gasoline, petrol, diesel etc

** Entropy (S) → State function
→ Extensive property

→ Defined to explain spontaniety of process.

→ It is measure of degree of of randomness or disorderness or patternless behaviour for maximum dissipation of Energy.

at a given Temp,

$\Rightarrow$ $S(gas) \ggg S(Liq.) > S(solid)$

$\Rightarrow$ for a Rx^n in System, no. of gaseous moles ↑es, S ↑es, $\boxed{\Delta S_{system} > 0}$

eg^n $\boxed{N_2 + 3H_2(g) \longrightarrow 2NH_3(g)}$; no. of gas molecules ↓es, S ↓es $\boxed{\Delta S < 0}$

eg^n $H_2(g) + I_2(g) \longrightarrow 2HI(g)$; $\boxed{\Delta S \approx 0}$

$\Rightarrow$ for isotopes, more Mass No. , $\boxed{\text{More } S}$

$C^{12}(g) \to C^{14}(g)$

$\Rightarrow$ Crystallization process $\Rightarrow$ liq. $\to$ Solid, S ↓es, $\Delta S < 0$

$\Rightarrow$ Melting of ice $\Rightarrow$ Solid $\to$ liq ; S ↑es, $\boxed{\Delta S > 0}$

☆ Imp

$\Rightarrow$ Boiling of egg $\Rightarrow$ S ↑es , $\Delta S > 0$

Due to High temp., protein molecules Breaks & no. of molecules ↑es ; So more randomness.

Denaturatn of Protein

Date ....

⇒ Stretching of Rubber / Spring

flexibility ↓es on Stretching, So S↓es, $\boxed{\Delta S < 0}$

2nd law of Thermodynamics :

Limitation of Ist Law → Energy change takes place But direction of change is not defined.

→ Process or Rx^n will move in that direction where Entropy of Universe is continously increasing

Universe ↓ Sys. + Surr.

for spontaneous process or feasible process (Irreversible)

$\boxed{\text{Total Entropy change} > 0}$ ⇒ for non-isolated system

Total ↓ Universe

$\Delta S_{system} + \Delta S_{surrounding} > 0$

$\boxed{\Delta S_{universe} > 0}$

or

$\Delta S_{Total} > 0$

for isolated system

$\boxed{\Delta S_{sys.} > 0}$ for spontaneity

Spontaneous process proceed in a particular dir^n until Total Entropy become max. & $\Delta S_{universe} = 0$

Spiral

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Reversible Rx^n or Process at Eq^n

$\boxed{\Delta S_{universe} = 0}$ S_{max} → for system

or

ΔS_{Total}

$\boxed{\Delta S_{system} = -\Delta S_{surrounding}}$

Non spontaneous or Non feasible process → constant external support is required

Entropy of universe must be decreasing in non-spont. direc^n.

$\boxed{\Delta S_{universe} < 0}$

More entropy, more stability of system at given temp.

Mathematically

Entropy change $(ds) = \frac{dq}{T}$

$$\boxed{\Delta S = \int ds = \int \frac{dq}{T}}$$

dq → Heat exchange b/w system & surrounding

$$\Delta S_{system} = \int \frac{dq_{system}}{T} \qquad \Delta S_{surr.} = -\int \frac{dq_{syst}}{T}$$

Date ....

(1) Phase Change PROCESS / reaction

$S \rightleftharpoons l$
or
$g \rightleftharpoons l$
or
$g \rightleftharpoons S$

→ occur at given T. and P.

$\boxed{q_p = \Delta H}$

$\Delta S = n \times \frac{\Delta H}{T}$

n → moles of substance

ΔH → Enthalpy of change

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

$\Delta H_{vap.} (H_2O, l) = x$ KJ/mole at 100°C

$$\boxed{\Delta S = \frac{x}{373} \; J/K}$$

(2) No Phase Change

$\boxed{q = nC\Delta T}$ only temp. changes

$\boxed{P = \text{constant}}$

$$\Delta S = \int \frac{dq_p}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC\,dt}{T}$$

C → Molar Heat capacity
→ Temp. dependent.

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But if Temp. dependency not given, then consider it to be independent of temp.

(*) If C_p temp. independent

$$\Delta S = nC \ln\left[\frac{T_2}{T_1}\right]$$

(3) For ideal gas in system

Changing its condition from

$$P_1, V_1, T_1 \longrightarrow P_2, V_2, T_2$$

$$\Delta S_{sys.} = \int \frac{dq}{T}$$

$$= \int \frac{dU + dPV}{T}$$

$$dq = dU + PdV$$
$$dU = dq - PdV$$
$$dU = dq + dw$$

$$\boxed{\Delta S_{sys.} = nC_v \ln\left[\frac{T_2}{T_1}\right] + nR \ln\left[\frac{V_2}{V_1}\right]}$$

$$\Rightarrow nC_v \ln\left[\frac{T_2}{T_1}\right] + nR \ln\left[\frac{P_1}{P_2} \times \frac{T_2}{T_1}\right]$$

$$= nC_v \ln\left[\frac{T_2}{T_1}\right] + nR \ln\left[\frac{P_1}{P_2}\right] + nR \ln\left[\frac{T_2}{T_1}\right]$$

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$$\Rightarrow n \ln\left[\frac{T_2}{T_1}\right](C_v + R) + nR\ln\left(\frac{P_1}{P_2}\right)$$

Also, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (Since moles of gas constant)

$$\boxed{\Delta S_{sys.} = nC_p \ln\left[\frac{T_2}{T_1}\right] + nR\ln\frac{P_1}{P_2}}$$

ΔS in various Process

① Isothermal Process $\Rightarrow T_1 = T_2$ $\qquad \ln\frac{T_2}{T_1} = 0$

ⓐ Reversible Process

Ideal gas

$$\Delta S = nR\ln\left[\frac{V_2}{V_1}\right] = -2.303\ nR\log\left(\frac{V_2}{V_1}\right)$$

or

$$nR\ln\left(\frac{P_1}{P_2}\right)$$

$$\Delta S_{system} + \Delta S_{surrounding} = 0$$

$$\Delta S_{surr.} = -\Delta S_{sys.}$$

$$= \boxed{-nR\ln\left(\frac{V_2}{V_1}\right) \quad \text{or} \quad -nR\ln\left(\frac{P_1}{P_2}\right)}$$

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(b) Irreversible isothermal process

$$\boxed{\Delta S_{Total} > 0}$$

Isothermal → $\Delta T = 0$

$\Delta U = 0 = nC_v\Delta T$

$\Delta H = 0 = nC_p\Delta T$

$$\boxed{\Delta S_{system} + \Delta S_{surrounding} > 0}$$

$$\Delta S_{sys.} = nR\ln\left(\frac{V_2}{V_1}\right)$$

or

$$nR\ln\left(\frac{P_1}{P_2}\right)$$

$$W_{irr} + q_{irr} = \cancel{\Delta U}^{\,0}$$

$$\boxed{-q_{irr} = W_{irr}}$$

$$\Delta S_{surr.} = \frac{(-q_{sys.})_{irr}}{T}$$

$$\Delta S_{surr.} = \frac{W_{irr}}{T}$$

$$\Rightarrow \frac{-P_{ext}(V_2 - V_1)}{T}$$

$$\Rightarrow -P_{ext}\left(\frac{nRT}{T}\right)\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$

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$$\boxed{\Delta S_{surr.} = -P_{ext} \times (nR) \times \left[\frac{1}{P_2} - \frac{1}{P_1}\right]}$$

Adiabatic Process

$q = 0$; $\boxed{\Delta S_{surr.} = 0}$ → whether rev or irr.

a) Reversible

$$\boxed{\Delta S_{sys.} = -\Delta S_{surr.}}$$

$$\boxed{\Delta S_{sys.} = 0 = \Delta S_{surr.}}$$

b) Irreversible

$\boxed{\Delta S_{sys.} > 0}$ $\boxed{\Delta S_{surr.} = 0}$

3) Isochoric

$V_1 = V_2$ $nR \ln \frac{V_2}{V_1} = 0$

for Ideal Gas

$$\boxed{\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right)}$$

4) Isobaric

$P_1 = P_2$

$$\boxed{\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)}$$

Date ....

** Gibbs free Energy (G) → state function, Ext property

→ Energy available in the system that can be used to obtain $\boxed{\text{Useful work}}$ under const. T, P.

→ non PV work
→ magnetic work
→ Electrical "
→ Rxⁿ

→ $\boxed{G = H - TS}$

(i) $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

(ii) $\Delta G_{sys} = -T\Delta S_{Total}$

→ Only defined for system

→ very useful Relatⁿ ⇒ $\boxed{dG = VdP - SdT}$

$\boxed{\text{only T const.}}$ $dT = 0$

⇓

Isothermal

$dG = VdP$

$dG = \frac{nRT}{P} dP$

**

$$\left(\frac{dG}{dt}\right)_P = -S \quad (dP=0)$$

$$\left(\frac{dG}{dP}\right)_T = V \quad (dT=0)$$

$$\boxed{\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)}$$

$$= nR \ln\left(\frac{V_1}{V_2}\right)$$

Spon. Process → will remain Spon. till S_{Total} becomes max. & G becomes min.

$\Delta S_{Total} > 0$

$\Delta G_{sys} < 0$

Spiral

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Rev. Process (at eq^n) $\Rightarrow S_{max}, G_{min}$

$$\boxed{\Delta S_{Total} = 0 \qquad \Delta G_{sys} = 0}$$

Non Spontaneous

$\Delta G_{sys.} > 0$

$\Delta S_{Total} < 0$

for Any Rx^n or Process in system

$$\Delta G_{sys} = \Delta H_{sys.} - T\Delta S_{sys.}$$

ΔG_{sys}	$\Delta H_{syst.}$	$\Delta S_{sys.}$
i) Always −ve (spontanteous at any temp.)	−ve (exo)	+ve
(ii) Always +ve (non spont. always)	+ve	−ve
(iii) $\lvert\Delta H\rvert > \lvert T\Delta S\rvert$ at low Temp. ΔG = −ve, Spon. $\lvert\Delta H\rvert < \lvert T\Delta S\rvert$ at High Temp. ΔG = +ve, Non-spon.	−ve	−ve

Date ....

		$\Delta H_{sys.}$	$\Delta S_{sys.}$
(iv) Spont. → $\Delta G = -ve$	at High Temp.	+ve	+ve
non-sp. → $\Delta G = +ve$	at low Temp.		

** Graphite to Diamond

$G \rightarrow D$ ordered ; $\Delta H = +ve$ (Endo)
$\Delta S = -ve$
$\Delta G = +ve$ (always)

$\boxed{\begin{array}{l}\Delta H = -ve \\ \Delta S = -ve\end{array}} \rightarrow \Delta G = \Delta H - T\Delta S$

ΔH: $-ve$; ΔS: $-ve$; $-T\Delta S$: $+ve$

Temp. at which Rx^n or Process Achieves Eq^n → usually Phase change

$\Delta G = 0 = \Delta H - T\Delta S$

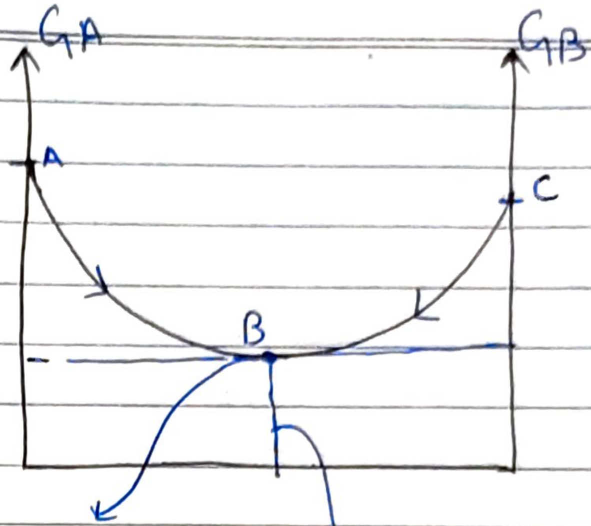
$$T = \frac{\Delta H}{\Delta S}$$

Rev. Rx^n → always achieves Eq^n

$A \rightleftharpoons B$

$\Downarrow$ $\Downarrow$

G_A G_B



Gmin $\rightarrow$ Eq^n point ΔG [illegible]

$\longrightarrow$ Progress of $\longleftarrow$
Rx^n w.r.t
time

$\boxed{\text{Sp. (Irr.)}}$

$\Delta S_{univ.} > 0$

$\Delta G_{sys} < 0$

Rev $\Rightarrow$ Eq^n $(S_{max})_{uni}$
Gmin

$$\boxed{\Delta S_{sys.} = \frac{\Delta H}{T}}$$

$$\Delta H_{sys.} - T\Delta S_{sys.} = \Delta G = 0$$

$$\Delta S_{Total} = 0$$

\# $\boxed{G = H - TS}$

at const. T, P

$$\boxed{\Delta G_{sys.} = \Delta H_{sys} - T\Delta S_{sys}}$$

\# $\boxed{dG = VdP - SdT}$ $G = f(T, P)$

Date ....

only T. const

$$\boxed{dG = VdP}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Const. P only

$$dG = -SdT$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$$

for Ideal gas

$$dG = \frac{nRT}{P}dP$$

$$\Delta G = \int dG = nRT\int \frac{dP}{P}$$

$$\boxed{\Delta G = nRT \ln \frac{P_2}{P_1}}$$

Rev. Rx^n

$$\underset{(g)}{aA} \rightleftharpoons \underset{(g)}{bB}$$

$$K_{eq} = Eq^n \text{ const.} = \frac{[B]^b}{[A]^a}$$

eg^n $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

$$K_{eq} = \frac{[N_2]^1[H_2]^3}{[NH_3]^2}$$

$[N_2]$ = molarity of N_2

$$= \frac{n_{N_2}}{\text{Vol. of container}}$$

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At Non-Eqⁿ point ⇒ Free Energy is still available

$\Delta G \neq 0$

⇒ Conc Ratio ≠ K_{eq}

⇒ $\boxed{\text{Conc Ratio} = \text{Reaction Quotient } (Q)}$

at given cond. of Rxⁿ — T, P

at Std. state

$\boxed{\Delta G} \neq \boxed{\Delta G^\circ}$

At Eqⁿ ⇒ $\Delta G = 0$, G min

$\Delta G^\circ \rightarrow$ may or may not be zero

$$\boxed{Q = K_{eq}}$$

$$\boxed{0 = \Delta G^\circ + RT \ln(K_{eq})}$$

$$\frac{-\Delta G^\circ}{RT} = \ln(K_{eq}) \qquad \frac{-\Delta G^\circ}{RT} = 2.303 \log(K_{eq})$$

$$\left(K_{eq} = e^{\frac{-\Delta G^\circ}{RT}}\right) \qquad \boxed{K_{eq} = 10^{\left(\frac{-\Delta G^\circ}{2.303RT}\right)}}$$

or

$$\boxed{K_{eq} = \text{antilog}\left(\frac{-\Delta G^\circ}{2.303RT}\right)}$$

Date ....

** Third law of Thermodynamics

"At 0K (Absolute zero) Entropy of perfectly crystalline substances is zero."

$$\boxed{S_{0\,kelvin} = 0}$$

Exception :-

Cl_2 (solid)
CO (solid)
NO (solid)
H_2O (solid)
H_2 (solid)

→ $S_{0K} \neq 0$

there must be some residual entropy due to random arrangement

H_2 (solid) ↓ due to existence of ortho & para form

CO CO CO
CO $\boxed{OC}$ CO → Randomness
CO CO $\boxed{OC}$

Due to 3rd law, Absolute value of entropy can be obtained provided molar Heat capacity is temp. dependent.

eg

Solid Sub (A) $\longrightarrow$ Solid Subst. (A)
0 K → T K

$$\Delta S = \int_{S(0K)}^{S(TK)} dS = n\int_{T_1=0K}^{T_2=TK} C\frac{dT}{T}$$

$\boxed{C \text{ can be like } aT^2 + bT}$

Spiral

Date ....

$$\boxed{S_{T\,K} - \cancel{S_{0\,K}}^{\,0} = n\int_{T_1}^{T_2} \frac{C\,dT}{T}}$$

Zeroth law of Thermo

If Body A & B are in thermal Eq^n, B & C are in thermal Eq^n, the A & C must be in thermal Eq^n.

$$T_A = T_B$$

$$T_B = T_C$$

then $\boxed{T_A = T_C}$